



Construction of titania–ceria nanostructured composites with tailored heterojunction for photocurrent enhancement

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Abstract

Titania–ceria (TiO₂–CeO₂) nanostructured composites based on the design of coating the surfaces of anodized TiO₂ nanotube arrays with small band gap CeO₂ nanoparticles have been constructed and characterized to demonstrate the effectiveness of the TiO₂–CeO₂ semiconductor heterojunction in enhancing the photocurrent response of TiO₂-based photoelectrodes. The TiO₂–CeO₂ heterojunction was confirmed to possess conduction and valence band offsets (0.81 and 1.59 eV, respectively) which promote the separation of photoinduced electron–hole pairs. The photocurrent densities of the TiO₂–CeO₂ composites prepared with low annealing temperatures were about 25–40% larger than that of the anatase TiO₂ nanotube arrays. When the nanoparticle-on-nanotube architecture of the TiO₂–CeO₂ heterostructure was maintained under specific processing conditions, the benefits of having a high specific surface area, a small band gap component capable of absorbing visible light, and a favorable heterojunction were achieved together for photocurrent enhancement.

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1. Introduction

Nanostructured assemblies or composites based on titania (TiO₂) have drawn significant attention in recent years due to their relevance in photocatalytic, semiconductor and solar cell applications.^{1–3} TiO₂ possesses several attractive characteristics for solar energy conversion, such as strong oxidizing activity, chemically stable, high photocorrosion resistance, and for nano-sized TiO₂, a large specific surface area for light absorption and photocatalytic reaction. Anatase and rutile are the two major crystalline phases of TiO₂ and possess relatively large band gaps of about 3.2 and 3.0 eV, respectively. A large number of studies have been dedicated to the improvement of the photocatalytic or photovoltaic properties of TiO₂ with a focus of enhancing visible light absorption by manipulating the absorption edge of TiO₂ via the addition of dopants.^{4–9} Methods to narrow the band gap of TiO₂ typically involve doping with transition metal ions, rare earth ions or anions such as N, C and S.^{4–9}

However, cationic dopants can give rise to concerns regarding chemical stability, carrier trapping and the formation of recombination centers.^{10,11} Anion doping, on the other hand, may need to be coupled with other techniques such as noble metal loading or the addition of electron donors/hole scavengers in order to achieve efficient photocatalytic performance.⁴ TiO₂ is commonly regarded as an oxygen-deficient oxide (i.e. TiO_{2-x}) with oxygen vacancy as the predominant defect.^{12,13} It has been shown that oxygen vacancies can result in the formation of extra electron energy levels in TiO₂, with energies in the range of 0.75–1.18 eV below the conduction band (CB).^{12–15} Aside from the doping approach, deliberate creation of oxygen vacancies by specific heat treatment has been demonstrated to be an alternative strategy to fundamentally improve the photocurrent response of TiO₂ across the visible region.^{16,17}

Aligned arrays of long TiO₂ nanotubes are often considered to be the optimal structure for solar energy conversion due to their high specific surface areas and continuous conduction pathways.^{2,18,19} The ability to fabricate high-quality TiO₂ nanotube arrays and control the architecture down to nanoscale dimensions can therefore significantly impact the scientific understanding and applications of TiO₂-based

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photoelectrodes and photocatalysts. One-dimensional TiO₂ nanotube arrays can be fabricated by the electrochemical anodization of titanium (Ti) in a fluoride-containing electrolyte – a simple process that requires no vacuum or high-temperature processing. The nanotubes grow as a result of competition between oxide formation via the electrochemical reaction and oxide dissolution by the fluoride ions.^{20,21} Since the anodized TiO₂ nanotubes are formed directly from downward oxidation and etching of the Ti substrate, the nanotubes are aligned and fixed onto the conductive Ti substrate. The employment of TiO₂ nanotube arrays in dye-sensitized and quantum-dot-sensitized solar cells as a wide band gap semiconducting layer^{2,22,23} and in photoelectrochemical cells (PEC) as a photoanode^{9,22} have been well documented. TiO₂–SrTiO₃ nanostructured composites based on growing large band gap SrTiO₃ nanoparticles on the surfaces of TiO₂ nanotube arrays for photoanode applications have been fabricated and characterized^{24,25} – the separation of photoinduced electron–hole (e[−]/h⁺) pairs is promoted by the TiO₂–SrTiO₃ semiconductor heterojunction, resulting in improved photoelectrochemical performance.

Coupling nanosized TiO₂ with a small band gap semiconductor material to create favorable band offsets at the material interface for charge carrier separation is an effective approach to build efficient photocatalytic or photoelectrode systems capable of absorbing visible light. If the CB edge of the small band gap material is more negative than that of TiO₂, visible light-excited CB electrons in the small band gap material will be injected to the large band gap TiO₂, resulting in a wide e[−]/h⁺ separation. The transfer of electrons is energetically favorable due to the CB offset and will effectively reduce the recombination of photoinduced charge carriers. Examples in the literature of TiO₂-based nanosized photocatalytic composites capable of visible light absorption include: mesoporous WO₃/TiO₂ thin films,²⁶ TiO₂ nanopowders coated with Bi₂S₃ or CdS nanopowders,²⁷ TiO₂ nanopowders coated with Cu₂O, Bi₂O₃ or ZnMn₂O₄ nanopowders²⁸ and anodized TiO₂ nanotube arrays covered with CdS quantum dots.²⁹ As for the above-described TiO₂–SrTiO₃ nanostructured composites,^{24,25} although they possess favorable band offsets at the material interface for charge carrier separation, both TiO₂ and SrTiO₃ are large band gap semiconductor materials with low absorption in the visible region. With the goal of designing an effective photocatalyst or photoelectrode under solar irradiation, a research task worthy of attention will therefore be the construction of a substrate-supported nanostructured composite consisting of anodized TiO₂ nanotube arrays and a small band gap material capable of visible light absorption. For such a composite, the presence of favorable band offsets at the material interface to promote the separation of photoinduced e[−]/h⁺ pairs is essential.

Ceria (CeO₂) is chosen in this study to be the small band gap component for the construction of TiO₂–CeO₂ nanostructured composites with an architecture characterized by coating anodized TiO₂ nanotube array surfaces with CeO₂ nanoparticles. CeO₂ is a technologically important oxide material due to its vast applications in fields such as catalyst and catalyst support,^{30,31} oxygen sensing³² and electrolyte or anode material in solid oxide fuel cells.^{33,34} Due to its fluorite structure,

diffusion of oxygen ions (O^{2−}) in crystalline CeO₂ is fast with the presence of oxygen vacancies. When the concentration of oxygen vacancies increases, the ease at which O^{2−} can move around in the crystal increases, allowing CeO₂ to reduce and oxidize molecules concurrently on its surface.³⁵ Nanocrystalline CeO₂ in particular has attracted much attention in photocatalysis research because of its small band gap of approximately 2.5–2.8 eV.^{36,37} It is clear from the preceding discussion that the successful fabrication of TiO₂–CeO₂ nanostructured composites with efficient visible light absorption by simple processing methods would be beneficial in the search for chemically stable and cost-effective photoelectrodes and photocatalysts operating under solar irradiation.

In this study, TiO₂–CeO₂ nanostructured composites were fabricated by a combination of anodization, hydrothermal and post-annealing methods. In order to further enhance the absorption in the visible region, the fabrication procedures were designed to promote the formation of oxygen vacancies in the composites. Our main goal was to investigate the optical absorption and photocurrent response of the TiO₂–CeO₂ nanostructured composites under irradiation with different wavelength ranges. Changes in the crystalline phase, microstructure and defect concentration of the composites with different processing conditions were characterized and related to the measured photoelectric properties. The electronic band structure of the TiO₂–CeO₂ semiconductor heterojunction was also determined to help us verify the benefits of forming the TiO₂–CeO₂ interface to the improvement of photoelectric properties. These tasks were achieved through the interpretation of characterization data from a variety of techniques, including X-ray diffractometry, scanning and transmission electron microscopies, X-ray and ultraviolet photoelectron spectroscopies, optical spectrophotometry and photocurrent analysis in a PEC.

2. Materials and methods

2.1. Synthesis of TiO₂ nanotube scaffold

Substrate-supported TiO₂ nanotube arrays, which are the main component and “scaffold” of the TiO₂–CeO₂ nanostructured composites, were fabricated by anodization of Ti foils in a standard two-electrode electrochemical cell. Ti foils of 0.1 mm thickness (Type 2N8, UMAT, Taiwan) were cleaned in an ultrasonic bath with acetone and isopropyl alcohol. Ethylene glycol (C₂H₆O₂, purity 99% plus, Acros Organics, USA) containing 0.3 wt% ammonium fluoride (NH₄F, purity 98% plus, Acros Organics, USA) and 5 vol% deionized water was used as the electrolyte for anodization. Anodization was carried out by applying a constant 20 V potential between the Ti foil (anode) and a platinum electrode (cathode) for 2 h, resulting in the formation of highly ordered amorphous TiO₂ nanotube arrays on the Ti foil substrate. The aligned nanotubes were fixed on and perpendicular to the conductive Ti substrate. Such a structural configuration is highly suitable for photoelectrode applications in photocatalytic reactions, such as water splitting and purification of pollutants. The amorphous TiO₂ nanotube arrays produced by anodization had an average tube length of

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